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| (54) Title: THERMOSET BINDER (57) Abstract A method of forming a mixture of a thermosetting binder and an inert material includes the steps of mixing an amine with an aldehyde at a suitable pH in a molar ratio of the aldehyde to the amine such that the aldehyde is in excess and an amine-aldehyde precondensate, which includes an aldehyde-substituted amine, is obtained, and mixing the precondensate with additional amine and the inert material to form the mixture of the thermosetting binder and the inert material. The aldehyde can be formaldehyde, which can be in the form of a mixture obtained by dissolving paraformaldehyde in methanol-containing formalin at a pH of at least 7. The invention extends to the use of an aqueous solution of formaldehyde stabilized with urea for the preparation of a thermosetting soil stabilizing composition, to a method of stabilizing soil, to soil stabilized in accordance with the method and to a solid artifact obtained from the settable material. | | |

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THERMOSET BINDER

THIS INVENTION relates to a thermoset binder. In particular, the invention relates to a method of forming a mixture of a thermosetting binder and an inert material, to the use of an aqueous solution of formaldehyde stabilized with urea, to a settable material, to a method of stabilizing soil, to soil stabilized in accordance with the method and to a solid artifact obtained from the settable material.

According to a first aspect of the invention, there is provided a method of forming a mixture of a thermosetting binder and an inert material, the method including the steps of

mixing an amine with an aldehyde at a suitable pH in a molar ratio of the aldehyde to the amine such that the aldehyde is in excess and an amine-aldehyde precondensate, which includes an aldehyde-substituted amine, is obtained; and

mixing the precondensate with additional amine and the inert material to form the mixture of the thermosetting binder and the inert material.

Typically, the aldehyde is formaldehyde and the amine and additional amine are urea, although melamine or other amines can also be used. The formaldehyde is typically in the form of formalin, which may include methanol.

The molar ratio in which the urea and the formaldehyde are mixed may be between 1:4 and 1:5. Preferably, the molar ratio in which the urea and the formaldehyde are mixed is between 1:4.5 and 1:5.

The formaldehyde may be in the form of a mixture obtained by dissolving paraformaldehyde in methanol-containing formalin at a pH of at least 7. Advantageously, this can be done without having to heat the dissolving paraformaldehyde. When the formaldehyde is obtained in this way, the pH of the formalin is preferably between 9 and 14.

The additional urea may be mixed with the precondensate (urea-stabilized formaldehyde) such that the molar ratio of total formaldehyde used to total urea used is between 4:1 and 1:1. Preferably the molar ratio of total formaldehyde used to total urea used is between 3:1 and 1:1, and most preferably between 2:1 and 1:1. It is to be noted that urea-formaldehyde resins having a molar ratio of urea: formaldehyde of greater than about 1:5 results in insoluble polymethylene-ureas that do not possess any adhesive properties.

The amine and the aldehyde may be mixed at a pH of between 5.5 and 8.5. Preferably, the pH is between 5.5 and 6.5.

As is well known to those skilled in the art, an amino resin comprising an amine and an aldehyde is formed by two reactions, an addition reaction and a condensation reaction. When urea and formaldehyde are used, the addition reaction, or hydroxymethylation, comprises addition of formaldehyde to the binding sides of the urea, and the extent of the hydroxymethylation depends on the urea to formaldehyde ratio. Urea has four binding sides located on the two

amine groups which each has two binding sides. In contrast, melamine has six binding sides. Thus, a maximum of four molecules of formaldehyde can bind to the binding sites of urea, and a maximum of six molecules of formaldehyde can bind to melamine. The condensation reactions only take place in acidic conditions and thus the time needed for the complete condensation reaction to take place decreases as the pH decreases. This also implies that shorter chain polymers will form which will give the amino resin a more crystalline texture.

An acid catalyst, e.g. sulphuric acid or citric acid, may be added to the precondensate and the additional amine. The acid may be weak or strong, organic or inorganic. If desired, water can also be added to provide the final mixture with a desired water content. The acid catalyst ensures that the binder obtained by mixing the precondensate and the additional amine has the correct pH to allow the desired chemical reactions to take place when the binder gels or sets. As is known by those skilled in the art, different polymeric products form at different reaction pH, particularly when the amino resin is prepared from formaldehyde in the form of formalin, and only some of these are useful as thermosetting binders in the field of the invention. However, for urea-stabilized formaldehyde, it has surprisingly been found that the properties of the amino resin do not change appreciably at a pH varying between about 4 and about 5.2. When formaldehyde reacts with urea the substitution of urea with carbonyl molecules are very much dependent on pH. Thus, the H^+ ion plays a role in chain formation (condensation reactions) and formaldehyde addition to urea (hydroxymethylation reaction), leading to different products being formed at different pH when formaldehyde and urea are reacted. When urea-stabilized formaldehyde is used, the H^+ ion is only involved in catalyzing chain growth, possibly explaining why only the reaction time, and not product properties, is influenced by pH.

The acid catalyst also speeds up the polymerization reaction to a desired level, and the pH controls the water permeability of the polymeric product. As will be appreciated, a too fast reaction may result in a solid resin before the

inert material is added or before a mixture of the thermosetting binder and inert material can be compacted, if so desired. A too slow polymerization reaction can lead to delay in construction time and lengthen the drying periods.

5 The binder obtained by mixing the precondensate and the additional amine may have a pH of between 3 and 6.5. Preferably, the binder has a pH of between 3.5 and 6, and most preferably between 3.5 and 5.

 All ingredients may be at a temperature of 50 °C or less, typically 30 °C or less, e.g. at ambient temperature.

10 The method may include mixing a functional ingredient selected from the group consisting of bitumen, bitumen emulsions, silicones, oils, silanes, anti corrosion agents, ultra violet light blocking agents, biocides, pH buffers, cement, ammonia, ammonium salts, plasticisers, and mixtures thereof with the precondensate and the additional amine.

15 Oils, bitumen, bitumen emulsions, silicone, silanes, or emulsions of these can act as waterproofing compounds. Plasticizers such as phthalates, hydrocarbons, acetates or glycols can add more suppleness and flexibility to an article, object or artifact produced from the mixture of the thermosetting binder and the inert material. Ultra violet light blocking agents such as organic phenols, phosphates or inorganic oxides are useful to stop ultra violet light degradation.
20 A biocide can prevent fungal or bacterial growth or inhibit such growth. The inert material may also include natural or synthetic fibers such as glass, steel, carbon or synthetic plastics or polymeric material fibers to provide added strength, or a thermoplastic resin to supplement or enhance certain properties of the mixture or to improve its resistance, strength and water insolubility.

25 The inert material may be selected from the group consisting of gravel, sand, soil, clay, silicas, particulate ore, rubber, stones, pebbles, partly

bound cementitious masses, grass, slag, waste dump material, coal particles, and mixtures thereof.

In one embodiment of the invention, the inert material is soil. The mass ratio of the thermosetting binder to the soil may be between 0.01 : 0.99 and 0.25 : 0.75. Typically, the mass ratio of the thermosetting binder to the soil is between 0.03 and 0.97. Similar mass ratios may be used for other types of inert material. The method may then include mixing a bitumen emulsion with the precondensate and the additional amine. The mixture of the thermosetting binder and the soil may have a moisture content of Optimum Moisture Content (OMC) for the particular soil plus or minus up to about 4 % by mass, preferably OMC plus or minus up to about 3 % by mass, e.g. up to OMC plus or minus about 2 % by mass. The binder and soil may be mixed by spraying the binder onto the soil and allowing the binder to permeate or penetrate into the soil, in which case the mixture of the binder and soil may have higher moisture contents, e.g. up to about 30 % moisture by mass.

The bitumen emulsion may comprise an anionic or cationic emulsifier, and may form between 1 % and 5 % by mass of the mass of the soil in the mixture.

According to a second aspect of the invention, there is provided the use of an aqueous solution of formaldehyde stabilized with urea for the preparation of a thermosetting soil stabilizing composition.

A soil stabilizing composition prepared from an aqueous solution of formaldehyde stabilized with urea advantageously has a much lower gel time than a thermosetting soil stabilizing composition prepared from formalin.

The molar ratio of urea to formaldehyde in the aqueous solution of urea-stabilized formaldehyde may be between 1:4 and 1:5. Preferably, the molar ratio is between 1:4.5 and 1:5.

5 The soil stabilizing composition may be prepared by mixing the aqueous solution of urea-stabilized formaldehyde with an amine selected from the group consisting of melamine, urea, and mixtures thereof.

In one embodiment of the invention, the amine is urea. The soil stabilizing composition may then have a pH of between 3 and 6.5, preferably between 3.5 and 6, and most preferable between 3.5 and 5.

10 Such an amino resin soil stabilizing composition can provide an increase in soil strength and soil volume stability and a decrease in water permeability.

15 The molar ratio of the total of the urea in the urea-stabilized formaldehyde and the urea mixed therewith to the formaldehyde in the urea-stabilized formaldehyde may be between 1:1 and 1:4, preferably between 1:1 and 1:3, and most preferably between 1:1 and 1:2, e.g. about 1:2.

The preparation of the soil stabilizing composition may include mixing an acid catalyst with the urea-stabilized formaldehyde solution and the amine. The acid catalyst may be as hereinbefore described.

20 The preparation of the soil stabilizing composition may include mixing a functional ingredient selected from the group consisting of bitumen, bitumen emulsions, silicones, oils, silanes, anti corrosion agents, ultra violet light blocking agents, biocides, pH buffers, cement, ammonia, ammonium salts, plasticisers, and mixtures thereof with the urea-stabilized formaldehyde and the amine. In one
25 embodiment of the invention, the functional ingredient is a bitumen emulsion.

The invention extends to a settable material comprising a mixture of a thermosetting binder and an inert material formed in accordance with a method as hereinbefore described.

The settable material can be compacted into a mold or into a desired shape, e.g. a brick, or it can be plastered. Thus, the settable material may be a building material.

According to a third aspect of the invention, there is provided a method of stabilizing soil, which includes

mixing an aqueous solution of urea-stabilized formaldehyde with an amine to form a thermosetting soil stabilizing composition; contacting the soil with the soil stabilizing composition; and allowing the soil stabilizing composition to set.

The method of stabilizing soil is particularly, though not necessarily exclusively suitable for hardening soils, sand, gravel or clay in the construction of roads, shelters, dams, canals and other artifacts or to stabilize soils, foundations, tunnels or the like. Thus, the method can be used to improve dirt roads or allow roads to be constructed with low cost black top, for the construction of driveways, parking lots, yards, pavements, paths and for pot-hole repairs. The method can be applied to walls, floors, and foundations of houses, schools, clinics, offices, factories, shops and sheds. Water storage devices such as dams, ponds, canals, tanks, river banks, dikes or the like can be waterproofed, better protected against erosion and treated to control mud. The method can be used to stabilize embankments, railway lines, underground grouting tunnels, basements, fenceposts, pylons, poles, pipes, landing strips and sports fields, and to form artificial rocks, statues or other decorative features.

The aqueous solution of urea-stabilized formaldehyde may be obtained by mixing urea with formaldehyde at a suitable pH in a molar ratio of the formaldehyde to the urea such that the formaldehyde is in excess.

The molar ratio of the urea to the formaldehyde may be between 1:4 and 1:5. Preferably the molar ratio is between 1:4.5 and 1:5, e.g. about 1:5.

The formaldehyde may be in the form of a mixture obtained by dissolving paraformaldehyde in methanol-containing formalin at a pH of at least 7, as hereinbefore described.

The urea and formaldehyde may be mixed at a pH of between 5.5 and 8.5, preferably between 5.5 and 6.5.

The amine may be urea, the urea being mixed with the aqueous solution of urea-stabilized formaldehyde such that the molar ratio of formaldehyde to total urea is between 1:1 and 4:1. Preferably, the molar ratio of formaldehyde to total urea is between 1:1 and 3:1, and most preferably between 1:1 and 2:1.

An acid catalyst may be mixed with the aqueous solution of urea-stabilized formaldehyde and the amine such that the soil stabilizing composition has a pH of between 3 and 6.5. Preferably, the soil stabilizing composition has a pH of between 3.5 and 6, and most preferably between 3.5 and 5.

Contacting the soil with the soil stabilizing composition may include mixing the soil stabilizing composition (as a liquid or a solid) and the soil in a mass ratio of between 0.01 : 0.99 and 0.25 : 0.75. The mixture of soil and soil stabilizing composition may have a moisture content of Optimum Moisture Content (OMC) for the particular soil plus or minus up to about 4 % by mass, preferably OMC plus or minus up to 3 about % by mass, e.g. OMC plus or minus about 2 % by mass. The soil stabilizing composition and soil may be contacted

by spraying the binder onto the soil and allowing the soil stabilizing composition to permeate or penetrate into the soil, in which case the mixture of the soil stabilizing composition and soil may have higher moisture contents, e.g. up to about 30 % moisture by mass.

5 The method may include mixing a bitumen emulsion as hereinbefore described with the aqueous solution of urea-stabilized formaldehyde and the amine.

The soil contacted with the soil stabilizing composition is typically compacted before the soil stabilizing composition sets.

10 The invention extends to soil stabilized in accordance with a method as hereinbefore described, and to a solid artefact obtained by shaping the settable material as hereinbefore described and allowing the settable material to set.

The invention will now be described, by way of the following non-limiting examples:

15 **EXAMPLE 1**

A 100 kg mixture of a thermosetting binder and an inert material (soil) was prepared by mixing the following ingredients together:

| | |
|------------------------------|-------------|
| urea-stabilized formaldehyde | 1000 grams |
| bitumen emulsion | 500 grams |
| phenol | 50 grams |
| urea | 80 grams |
| citric acid | 5 grams |
| water | 2000 grams |
| soil | 96365 grams |

The urea-stabilized formaldehyde solution used was Inkunite UFC (registered trade mark) obtained from Resinkem (Pty) Limited, Umbogintwini, South Africa, 4120. The Inkunite had a formaldehyde content of between 51 and 58 % by mass, a urea content of between 22 and 28 % by mass and a pH of between 6.5 and 8. The bitumen emulsion had a bitumen concentration of about 60 %. The soil included fine sand and had a moisture content of about 5 %.

The mixture of the abovementioned ingredients was formed into the shape of bricks, compacted, and left to dry, set and harden at room temperature.

EXAMPLE 2

Soil was stabilized as follows:

12.5 g of Inkunite, 7.5 g urea, 40 g of water and 20 g of a bitumen emulsion were added together and thoroughly mixed. An acid catalyst, in the form of citric acid, was added to lower the pH to be between 3 and 4.5. The resultant soil stabilizer composition was added to 1 kg of soil and mixed well into the soil to obtain a good distribution of the soil stabilizer throughout the soil. Water was added to bring the total moisture content of the mixture of the soil stabilizer composition and the soil to the optimum moisture content for the soil for the specific compactive effort that would be used for the mixture of the soil stabilizer composition and the soil. The mixture was then compacted in conventional manner and allowed to dry, set and harden at room temperature.

EXAMPLE 3

Experiments were conducted to compare the thermosetting binders produced by using formalin and Inkunite. 22 g of formalin and Inkunite respectively was mixed with 13 g of urea and 0.0065 g of citric acid. The pH of the Inkunite used was 5.45 and that of the formalin was 3.85. The formalin

comprised 37 % formaldehyde and 7 % methanol. Three different mixtures were prepared and left to react. The first mixture was made from Inkunite, had an end pH of 5.45 and the urea : formaldehyde molar ratio was 1:1.4. The second mixture was made from formalin, had an end pH of 5.45 and the urea : formaldehyde molar ratio was 1:1.25. The third mixture was also prepared from formalin, had an end pH of 3.85 and the urea : formaldehyde molar ratio was also 1 : 1.25. Raman spectra of the final set products were taken and the gel time of each mixture was measured.

The first mixture had a gel time of 615 minutes, the second mixture had a gel time of 1400 minutes and the third mixture had a gel time of 65 minutes. As will be noticed, although the first mixture and the second mixture had the same pH, the gel time of the first mixture, prepared from Inkunite was much less than the gel time of the second mixture prepared from formalin. The experiments also clearly illustrate the drastic effect of pH. The Raman spectra for the three mixtures showed that there were only a few differences in the spectra of the three amino resins formed.

EXAMPLE 4

This example illustrates the preparation of an aqueous solution of urea-stabilized formaldehyde. This example also illustrates that it is possible to prepare such a urea-stabilized formaldehyde precondensate on a building site, at ambient temperature using formalin and paraformaldehyde.

Commercially available urea-formaldehyde precondensate, such as Inkunite is manufactured from urea and formalin by letting the hydroxymethylation reaction take place to a certain extend at an alkaline pH and then, by rendering the solution acidic, to let the condensation take place. The solution is again made alkaline and acidic to let the total reaction proceed to a specific limit. Excess

water is then removed and the liquid resin purified in four distillation columns in series.

In contrast to the above commercial procedure, urea formaldehyde precondensate mixtures were prepared by dissolving 10 g of paraformaldehyde and 20 g of mixtures containing methanol and formalin and adjusting the pH of the mixtures to about 10. The 20 g mixtures of methanol and formalin contained different methanol concentrations varying between 7 % and 50 %.

In each case, after 5 minutes of stirring, urea was added to the mixtures and the stirring continued for a total of 2 hours. Thereafter the liquid, if any, was removed and the amount of paraformaldehyde not dissolved was separate, dried and weighed.

The experiments showed that there is a clear correlation between the methanol content of the methanol-formalin mixture and the solubility of the paraformaldehyde in the formalin, the solubility of paraformaldehyde increasing with increasing methanol content. One possible reason for this could be that more methanol increases the splitting of the paraformaldehyde chain into its monomers. The experiment was extended by determining the shelf life of the precondensate prepared, after water was evaporated to provide a precondensate having a water content of about 20% by mass. The shelf life was found to be about 4 days, and was found to be mostly independent of the pH of the precondensate in the pH range of 6 to 8. The shelf life was defined as the time it took for the clear precondensate to become cloudy.

EXAMPLE 5

The influence of pH on amino resin properties and gel time was investigated at a fixed urea : formaldehyde molar ratio of 1:1.4 by preparing mixtures of urea and Inkunite and then adjusting the pH step by step downwards

by adding citric acid. The effect of pH on resin properties were investigated at pH 4.2, 4.5, 4.9 and 5.2 and the gel time was measured for each pH mixture. The amino resin products were left to dry for about 2 days and then visually compared.

5 It was found that the gel time increases drastically with increasing pH, being about 50 minutes at a pH of 4.5 and about 520 minutes at a pH of 5.2. However, the amino resin products formed at different pH were similar, all being very hard, very homogeneous and not very crystalline. All had excellent water resistance. This is in contrast with the properties of amino resins formed at
10 different pH from formaldehyde and urea, which ranges from a white solid through a gel to a precipitate with increasing pH.

EXAMPLE 6

20 g of paraformaldehyde was dissolved in 40 g of a mixture containing equal amounts of methanol and formalin and the pH was adjusted to
15 about 10 with NaOH. After 5 minutes of stirring 10 g urea was added to the mixture and stirring continued for 2 hours. A number of samples with different pH were then prepared, ranging between a pH of 5 and a pH of 7.5 at 0.5 pH intervals. After 24 hours the samples were compared. After 1 month, 22 g of each of the samples that were clear and stable were reacted with 13 g urea each
20 and the pH adjusted to 4.2. The final products were compared with amino resins prepared from urea and formaldehyde at a pH of 4.2.

It was found that, in all cases except for pH 5.5 and 6, a solid product was formed. Thus, at pH lower than 5 a normal condensed amino resin formed, and at high pH monomethylolurea or dihydroxymethylurea formed. Only
25 at pH 5.5 and 6 did a viscous liquid form that had a shelf life of more than a month. When 22 g of these liquids was respectively added to 13 g of urea and

the pH adjusted to 4.2 a smooth, hard product formed without any cracks in both cases.

EXAMPLE 7

The influence of urea : formaldehyde molar ratio on amino resins prepared from urea-stabilized formaldehyde is illustrated in this Example.

30 g of urea was added to Inkunite to provide a urea : formaldehyde molar ratio of 1:2 and the pH of the resultant mixture was measured at 5.12. A small quantity of citric acid as a source of free hydrogen ions were added. In a similar manner, a mixture with a molar ratio of 1:1.4 was prepared, and the viscosity and gel time of the mixtures were measured. The resultant amino resins were left to dry for 2 days and their properties visually compared.

It was found that the 1:2 molar ratio mixture reacted quickly to become a gel, but took three days to solidify. The 1:1.4 molar ratio mixture gelled and solidified quicker. The 1:2 molar ratio product was very smooth, hard and had no cracks. The 1:1.4 molar ratio product was more brittle and had small cracks. Both products became soft when placed in water, but hardens again when dried. The 1:2 molar ratio product had much better water resistance, which can possibly be attributed to the fact that the water is slowly displaced from the resin as the cross linking starts, while when the cross linking occurs quickly, the water is trapped inside the resin matrix and due to adhesion forces the resin can crack and become brittle.

An advantage of the 1:2 molar ratio resin is that it requires 40% less urea than the 1:1.4 molar ratio resin, which has raw material cost and transport cost implications.

EXAMPLE 8

A series of tests were conducted to determine the effectiveness of a cold-setting amino resin prepared from urea-stabilized formaldehyde and urea (referred to as resin A) with that of a cold-setting amino resin prepared from formaldehyde and urea (referred to as resin B). Resin A was prepared using 1.67 g Inkunite per gram urea. Resin B was prepared using 1.67 g formalin (37 % formaldehyde and 7 % methanol) per gram urea. When bitumen was used, an anionic bitumen emulsion (SS60) was used.

The liquid resin was mixed with the soil, compacted and then subjected after some time to the indirect tensile strength (ITS) test. The soil was a dark brown shale and fine gravel mixture 95 % of which passed through a 13.2 mm screen. It had an optimum moisture content of 9.6 %, a hygroscopic moisture content of 2.6 % and a maximum dry density of 1985 kg/m³. A Marshall apparatus was used for the ITS tests and samples were compacted using 75 blows for bituminous mixtures and 50 blows for other mixtures in standard molds of 101.6 mm inside diameter. For wet strength tests, the samples were soaked for 24 hours in water. All test were conducted at 23 degrees Celsius and 85 kPa atmospheric pressure.

The tests showed that soils stabilized with resin A and resin B which included bitumen had the same initial increase in strength, but the addition of bitumen results in a higher maximum strength for the stabilized soil. The maximum strength results within about 7 to 24 days, after all the water has evaporated from the samples.

Resin A stabilized soil initially had a lower dry strength than resin B stabilized soil, but later on increased to values even higher than those of resin B stabilized soil. However, resin A with bitumen stabilized soil had a much lower

wet strength than resin B with bitumen stabilized soil. Wet and dry strength for both resin stabilized soils reached an optimum when the soil was at its optimum moisture content (OMC), irrespective of the presence of bitumen.

5 Both the wet and dry strength of the stabilized soil samples increased with increasing dosages of resin A and resin B, but reached a limit (at about 5 % by mass) for dry strength where addition of more resin did not increase the dry strength.

10 For both resin A and resin B the strength of the stabilized soil increased as the reaction pH was lowered from 7 to about 4, and this increase was enhanced by the addition of bitumen emulsion. However, the effect of bitumen on the dry strength of soil stabilized with resin A was marginal.

At an urea : formaldehyde molar ratio of 1:2 the dry strength of both resin A and resin B stabilized soil samples reached an optimum. The wet strength improved at higher molar ratios for resin A stabilized soil samples.

15 It is an advantage of the invention that urea-stabilized formaldehyde can be used, resulting in less formaldehyde fumes being produced, a more neutral pH being employed, more predictable evenly cross linked polymers being formed, improved user and ecological friendliness and less transport costs due to lower water content and lower flammability. A soil stabilizing composition made in
20 accordance with the invention advantageously has a shorter gel time than a conventional urea formaldehyde soil stabilizing composition. A further advantage is that paraformaldehyde can be used to prepare urea-stabilized formaldehyde.

CLAIMS:

1. A method of forming a mixture of a thermosetting binder and an inert material, the method including the steps of

5 mixing an amine with an aldehyde at a suitable pH in a molar ratio of the aldehyde to the amine such that the aldehyde is in excess and an amine-aldehyde precondensate, which includes an aldehyde-substituted amine, is obtained; and

mixing the precondensate with additional amine and the inert material to form the mixture of the thermosetting binder and the inert material.

10 2. A method as claimed in claim 1, in which the aldehyde is formaldehyde.

3. A method as claimed in claim 2, in which the amine is urea.

4. A method as claimed in claim 3, in which the molar ratio in which the urea and the formaldehyde are mixed is between 1:4 and 1:5.

15 5. A method as claimed in any one of claims 2 to 4 inclusive, in which the formaldehyde is in the form of a mixture obtained by dissolving paraformaldehyde in methanol-containing formalin at a pH of at least 7.

20 6. A method as claimed in any one of claims 2 to 5 inclusive, in which the additional urea is mixed with the precondensate such that the molar ratio of total formaldehyde used to total urea used is between 1:1 and 4:1.

7. A method as claimed in claim 6, in which the molar ratio of total formaldehyde used to total urea used is between 1:1 and 2:1.

8. A method as claimed in any one of the preceding claims, in which the amine and the aldehyde are mixed at a pH of between 5.5 and 8.5.

9. A method as claimed in any one of the preceding claims, in which an acid catalyst is added to the precondensate and the additional amine.

5 10. A method as claimed in any one of the preceding claims, in which the binder obtained by mixing the precondensate and the additional amine has a pH of between 3 and 6.5.

11. A method as claimed in any one of the preceding claims, in which all ingredients are at a temperature of 30 °C or less.

10 12. A method as claimed in any one of the preceding claims, which includes mixing a functional ingredient selected from the group consisting of bitumen, bitumen emulsions, silicones, oils, silanes, anti corrosion agents, ultra violet light blocking agents, biocides, pH buffers, cement, ammonia, ammonium salts, plasticisers, and mixtures thereof with the precondensate and the additional
15 amine.

13. A method as claimed in any one of the preceding claims, in which the inert material is selected from the group consisting of gravel, sand, soil, clay, silicas, particulate ore, rubber, stones, pebbles, partly bound cementitious masses, grass, slag, waste dump material, coal particles, and mixtures thereof.

20 14. A method as claimed in any one of the preceding claims, in which the inert material is soil, the mass ratio of the thermosetting binder to the soil being between 0.01 : 0.99 and 0.25 : 0.75.

15. A method as claimed in claim 14, which includes mixing a bitumen emulsion with the precondensate and the additional amine.

16. A method as claimed in claim 14 or claim 15, in which the mixture of the thermosetting binder and the soil has a moisture content of Optimum Moisture Content (OMC) for the particular soil plus or minus up to 4 % by mass.

17. Use of an aqueous solution of formaldehyde stabilized with urea for the preparation of a thermosetting soil stabilizing composition.

18. Use as claimed in claim 17, in which the molar ratio of urea to formaldehyde in the aqueous solution of urea-stabilized formaldehyde is between 1:4 and 1:5.

19. Use as claimed in claim 17 or claim 18, in which the soil stabilizing composition is prepared by mixing the aqueous solution of urea-stabilized formaldehyde with an amine selected from the group consisting of melamine, urea, and mixtures thereof.

20. Use as claimed in claim 19, in which the amine is urea, the soil stabilizing composition having a pH of between 3 and 6.5.

21. Use as claimed in claim 20, in which the molar ratio of the total of the urea in the urea-stabilized formaldehyde and the urea mixed therewith to the formaldehyde in the urea-stabilized formaldehyde is between 1:1 and 1:4.

22. Use as claimed in any one of claims 17 to 21 inclusive, in which the preparation of the soil stabilizing composition includes mixing an acid catalyst with the urea-stabilized formaldehyde solution and the amine.

23. Use as claimed in any one of claims 17 to 22 inclusive, in which the preparation of the soil stabilizing composition includes mixing a functional ingredient selected from the group consisting of bitumen, bitumen emulsions, silicones, oils, silanes, anti corrosion agents, ultra violet light blocking agents,

biocides, pH buffers, cement, ammonia, ammonium salts, plasticisers, and mixtures thereof with the urea-stabilized formaldehyde and the amine.

24. Use as claimed in claim 23, in which the functional ingredient is a bitumen emulsion.

5 25. A settable material comprising a mixture of a thermosetting binder and an inert material formed in accordance with a method as claimed in any one of claims 1 to 16 inclusive.

10 26. A method of stabilizing soil, which includes
mixing an aqueous solution of urea-stabilized formaldehyde
with an amine to form a thermosetting soil stabilizing composition;
contacting the soil with the soil stabilizing composition; and
allowing the soil stabilizing composition to set.

15 27. A method as claimed in claim 26, in which the aqueous solution of urea-stabilized formaldehyde is obtained by mixing urea with formaldehyde at a suitable pH in a molar ratio of the formaldehyde to the urea such that the formaldehyde is in excess.

28. A method as claimed in claim 26 or claim 27, in which, the molar ratio of the urea to the formaldehyde is between 1:4 and 1:5.

20 29. A method as claimed in claim 27 or claim 28, in which the formaldehyde is in the form of a mixture obtained by dissolving paraformaldehyde in methanol-containing formalin at a pH of at least 7.

30. A method as claimed in claim 27, in which the urea and formaldehyde are mixed at a pH of between 5.5 and 8.5.

31. A method as claimed in any one of claims 26 to 30 inclusive, in which the amine is urea, the urea being mixed with the aqueous solution of urea-stabilized formaldehyde such that the molar ratio of formaldehyde to total urea is between 1:1 and 4:1.

5 32. A method as claimed in claim 31, in which the molar ratio of formaldehyde to total urea is between 1:1 and 2:1.

10 33. A method as claimed in any one of claims 26 to 32 inclusive, in which an acid catalyst is mixed with the aqueous solution of urea-stabilized formaldehyde and the amine such that the soil stabilizing composition has a pH of between 3 and 6.5.

15 34. A method as claimed in any one of claims 26 to 33 inclusive, in which contacting the soil with the soil stabilizing composition includes mixing the soil stabilizing composition and the soil in a mass ratio of between 0.01 : 0.99 and 0.25 : 0.75, the mixture of soil and soil stabilizing composition having a moisture content of Optimum Moisture Content (OMC) for the particular soil plus or minus up to 4 % by mass.

35. A method as claimed in any one of claims 26 to 34 inclusive, which includes mixing a bitumen emulsion with the aqueous solution of urea-stabilized formaldehyde and the amine.

20 36. A method as claimed in any one of claims 26 to 35 inclusive, in which the soil contacted with the soil stabilizing composition is compacted before the soil stabilizing composition sets.

37. Soil stabilized in accordance with a method as claimed in any one of claims 14 to 16 inclusive or any one of claims 26 to 36 inclusive.

38. A solid artefact obtained by shaping the settable material as claimed in claim 25 and allowing the settable material to set.

39. A method of forming a mixture of a thermosetting binder and an inert material as claimed in claim 1, substantially as herein described and illustrated.

5 40. Use as claimed in claim 17 of an aqueous solution of formaldehyde stabilized with urea, substantially as herein described and illustrated.

41. A settable material as claimed in claim 25, substantially as herein described and illustrated.

10 42. A method of stabilizing soil as claimed in claim 26, substantially as herein described and illustrated.

43. Stabilized soil as claimed in claim 37, substantially as herein described and illustrated.

44. A solid artefact as claimed in claim 38, substantially as herein described and illustrated.

15 45. A new method of forming a mixture of a thermosetting binder and an inert material, a new use of urea-stabilized formaldehyde, a new settable material, a new method of stabilizing soil, new stabilized soil, or a new solid artefact, substantially as herein described.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/IB 00/00007

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K17/28 C09K17/48 C09K17/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|---|
| X | <p>GB 1 184 129 A (TOYO KOATSU INDUSTRIES) 11 March 1970 (1970-03-11)</p> <p>page 1, line 70 -page 2, line 20 page 2, line 60 - line 121 page 3, line 38 - line 53</p> <p style="text-align: center;">— -/-</p> | <p>1-3, 9, 12-14, 19, 20, 22, 23, 26, 27, 33, 34, 37, 39-43, 45</p> |

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.*** Special categories of cited documents:**

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Boulon, A

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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International Application No

PCT/IB 00/00007

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| GB 1194227 A | 10-06-1970 | NONE | |
| JP 45024951 B | | NONE | |
| JP 46004786 B | | NONE | |
| JP 55011713 B | 12-01-1974 | JP 1021790 C JP 49003411 A | 25-11-1980 12-01-1974 |